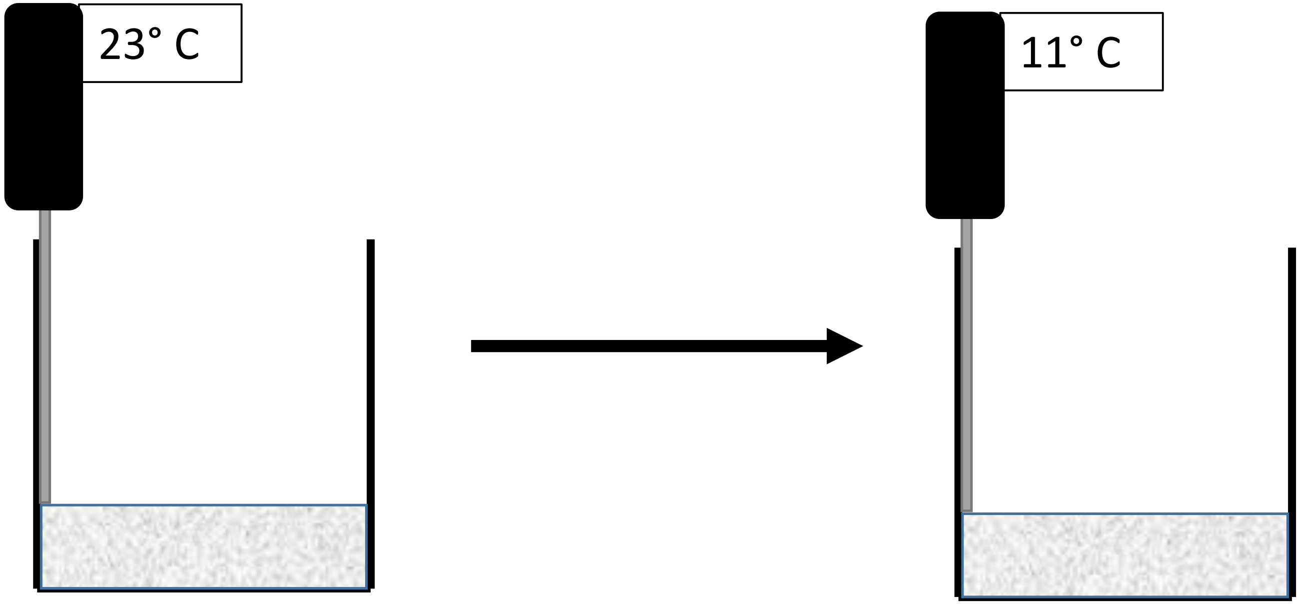
Topics to cover

1. Heats of reaction
2. Calorimetry
3. Enthalpy
4. Thermochemical equations
5. Bond Energy

Exchange of Heat between System and Surroundings

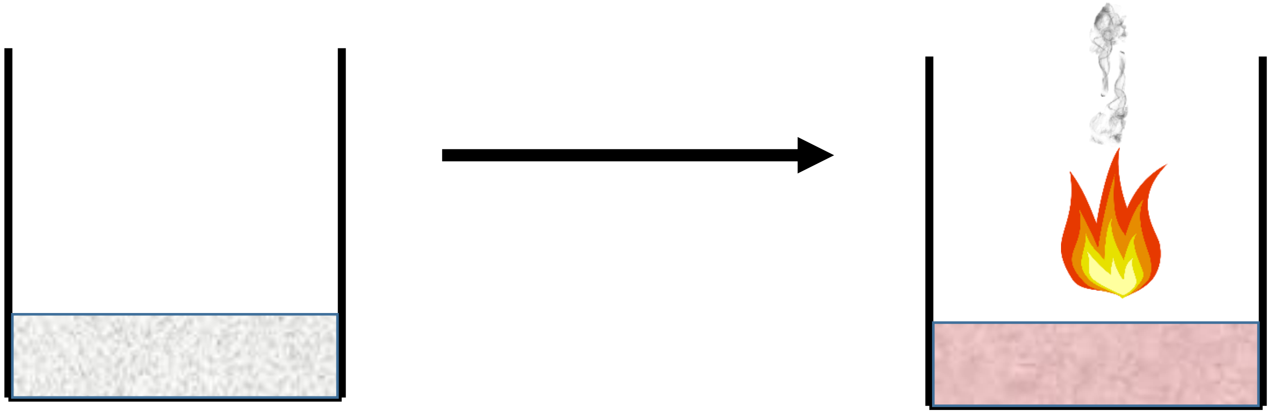
$Ba(OH)_2 \cdot 8H_2O + 2\ NH_4SCN \rightarrow Ba(SCN)_2 + 2\ NH_3 + 10\ H_2O$



- Temperature of beaker and surrounding air drops.
- When heat is absorbed by the system from the surroundings, the process is **endothermic**.

Exchange of Heat between System and Surroundings

$$2\ K + 2\ H_2O \rightarrow 2\ KOH + H_2$$



- Heat flows violently from system to surrounding.
- Temperature of beaker and surrounding air increases.
- When heat is released by the system into the surroundings, the process is **exothermic**.

Other examples

- Combustion of Hydrogen gas in oxygen

$H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (l)$ + Energy (heat)

Exothermic reaction

- Decomposition of mercuric oxide at high temperature

Energy (heat) + $2HgO\ (s) \rightarrow 2\ Hg\ (l) + O_2\ (g)$

Endothermic reaction

HEAT IS NOT REALLY A REACTANT OR PRODUCT!

*SI unit for energy is Joule (J)

Can also be measured in calories (1 calorie = 4.184 Joule)

Heat of Reaction (H)

- Also known as **Enthalpy of Reaction.**
- It is a thermodynamic unit of measurement useful for calculating the amount of energy per mole either released or produced in a reaction.
- Enthalpy is defined as

$$\mathbf{H = E + PV}$$

Where

E = Internal energy

P= pressure of the system

V = volume of the system

- Since enthalpy is derived from P, V and E, all of which are state functions, enthalpy is also a **state function.**
- At constant pressure:

$$\Delta H = \Delta E + P\Delta V$$

Relationship between Enthalpy and Energy

- If a system absorbs energy (E + q) and uses some of the internal energy to do work (-w) then:

$$\Delta E = q - w$$

- At constant pressure, work done is PΔV

$$\Delta E = q_p - P\Delta V$$

$$\text{SO } q_p = \Delta E + P\Delta V \qquad \text{eqn (I)}$$

- The change in enthalpy at constant pressure is

$$\Delta H = \Delta E + P\Delta V \qquad \text{eqn (II)}$$

- Comparing eqns I and II means heat absorbed at constant pressure is equal to enthalpy change:

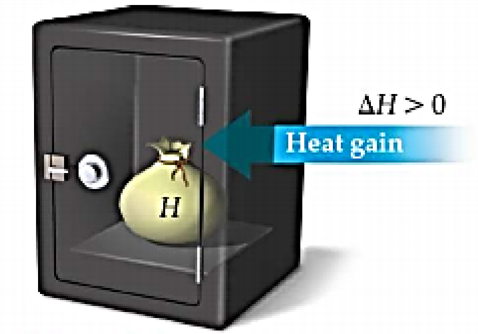
$$\Delta H = q_p$$

*per mole

Endothermic and Exothermic

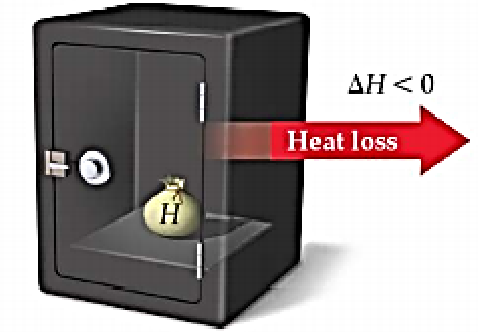
$\Delta H = H_{final} - H_{initial}$ or $\Delta H = H_{products} - H_{reactants}$

Constant pressure maintained in system



(a) An endothermic reaction

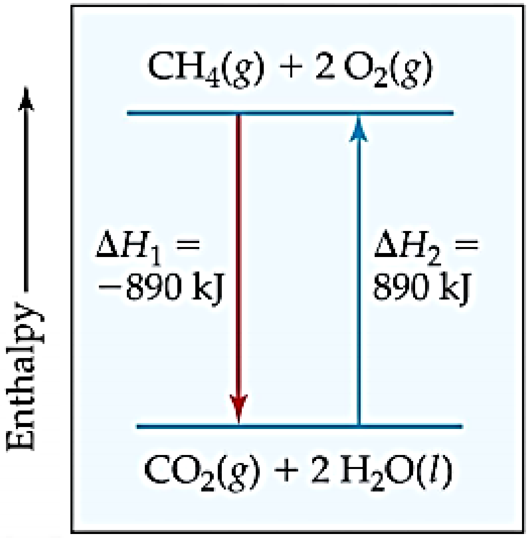
- A process is **endothermic** when ΔH is positive (>0).

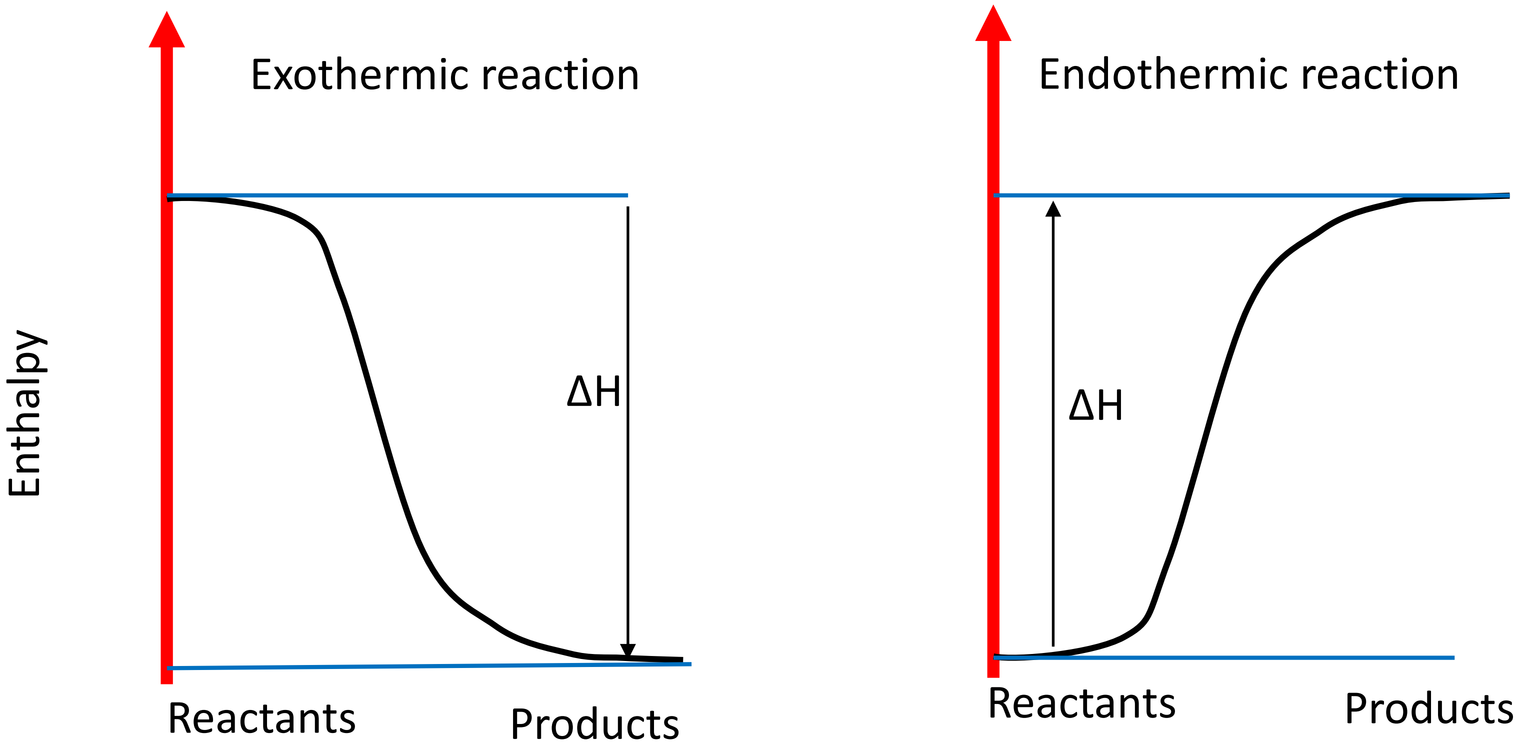


(b) An exothermic reaction

ΔH is amount of heat that flows into or out of system under constant pressure.

- A process is **exothermic** when ΔH is negative (<0).





Energy diagram

Heat flow

If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative.

Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive.

Thus $\boldsymbol{\Delta H_{rxn}} < 0$ *for an exothermic reaction*,
and $\boldsymbol{\Delta H_{rxn}} > 0$ *for an endothermic reaction*.

ΔH_{rxn}

- Defines the change in the enthalpy of a chemical reaction that occurs at a constant pressure.
- Reactants have a definite total enthalpy $H_{(reactants)}$
- Products have a definite total enthalpy $H_{(products)}$
- Therefore for a chemical reaction enthalpy change is:

$$\Delta H = H_{(products)} - H_{(reactants)}$$

Example

- We can calculate ΔH of the reaction:

$$CH_4\ (g) + 2\ O_2\ (g) \rightarrow CO_2\ (g) + 2\ H_2O\ (l)$$

Given the following enthalpies per mole:

CH_4 (g) = -75.0 KJ

O_2 (g) = 0.0 KJ

CO_2 (g) = -393.0 KJ

H_2O (l) = -286.0 KJ

CH_4 (g) + 2 O_2 (g) → CO_2 (g) + 2 H_2O (l)

$\Delta H = H_{(products)} - H_{(reactants)}$

ΔH = (Enthalpy of 1 mol CO_2 + Enthalpy of 2 moles of H_2O) – (Enthalpy of 1 mol of CH_4 + Enthalpy of 2 moles of O_2)

ΔH = (-393.0 + 2(-286)) KJ – (-75 + 2 (0.0)) KJ

ΔH = -890 KJ

Calorimetry

Calorimetry

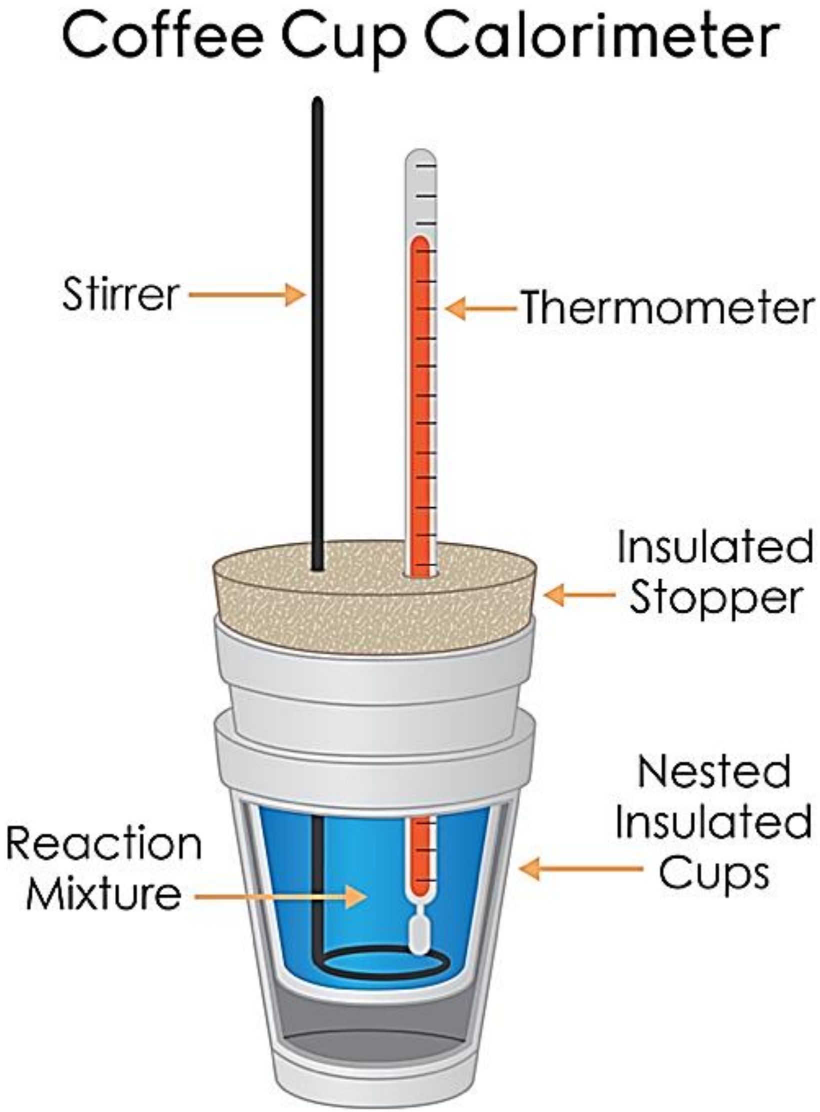
- Calorimetry is a technique for measuring heat and enthalpy changes in chemical reactions.
- **calorimeter** is the device used to measure heat.
- The quantity of heat transferred by the reaction causes a change in temperature of the solution.

Types of calorimeters

1. **Constant pressure calorimeters** - Coffee cup calorimeter

A coffee cup calorimeter is made of Styrofoam.

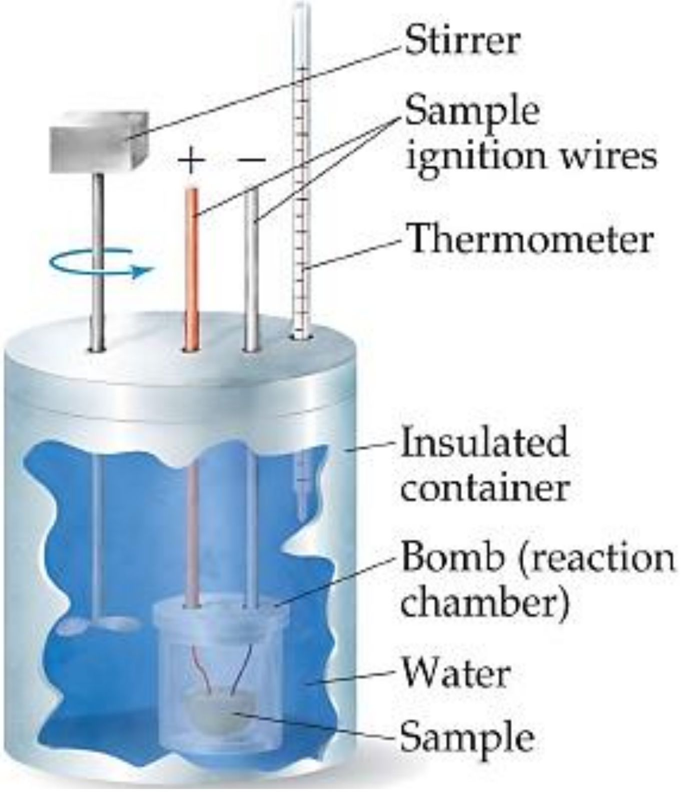
(Assume $q_{styrofoam} = 0$)



Types of calorimeters

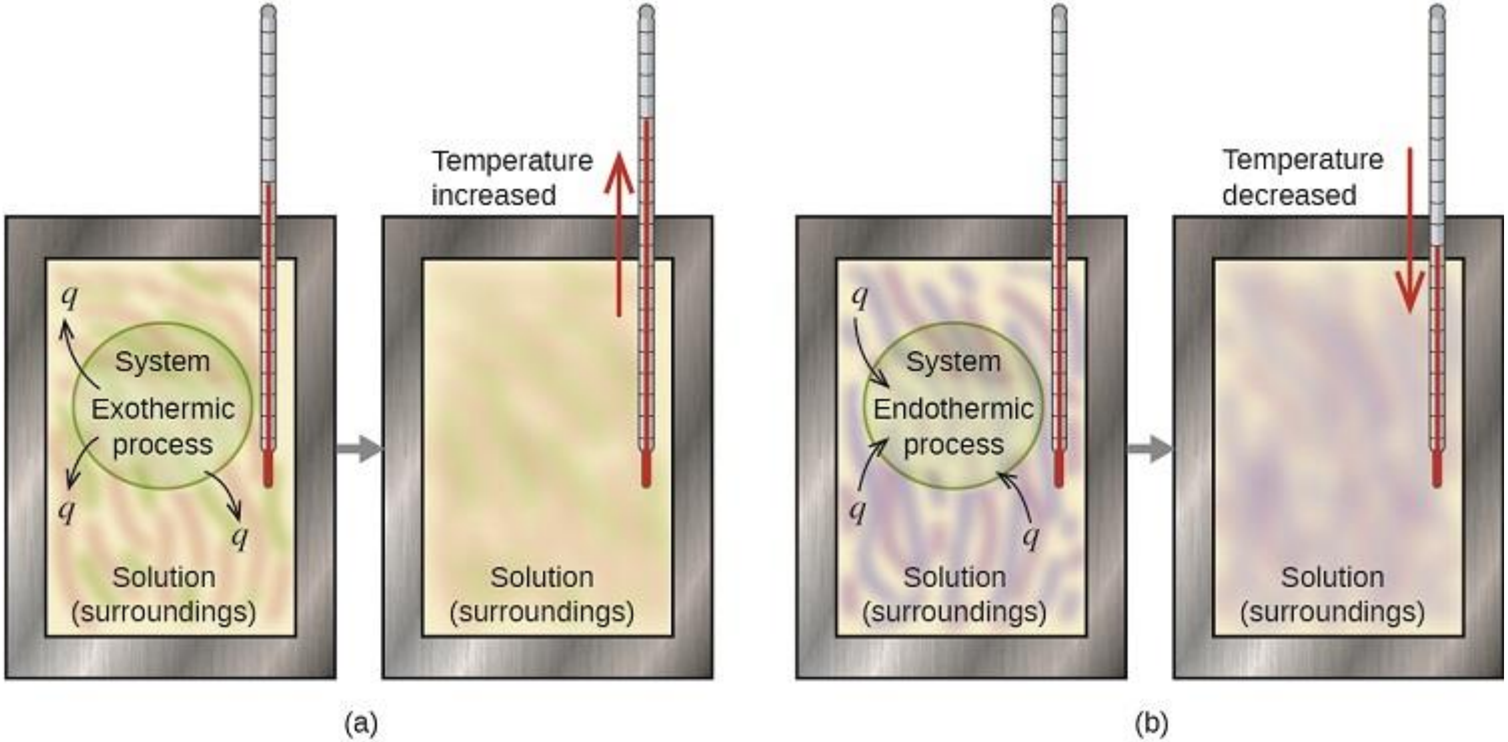
2. Constant volume calorimeters - Bomb calorimeters

Water and bomb calorimeter material (metal) can absorb heat.



System and surroundings in a calorimeter

- System - the substance or substances undergoing the chemical or physical change
- Surrounding - the solution or other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system



Basics of calorimetry

- Conservation of energy requires that

$$q_{system} + q_{surrounding} = 0$$

- Therefore

$$q_{system} = - q_{surrounding}$$

- The negative sign only shows the q_{system} and $q_{surrounding}$ are in opposite direction of heat flow.

Heat capacity , C

- Heat capacity is the amount of heat required to raise the temperature of a given amount of substance by 1 ^{o}C or 1 K.

$$\mathbf{q = C \times \Delta \mathit{T}}$$

q = heat lost or gained
C = heat capacity
$\Delta T = T_{\text{final}} - T_{\text{initial}}$

Units for heat capacity: J $^{o}C^{-1}$ or J K^{-1}

Specific heat capacity, c

- **Specific heat capacity** is the amount of heat required to raise the temperature of **1 gram** of a substance by 1 ^{o}C or 1 K.

$$\boldsymbol{q = c \times m \times \Delta T}$$

q = heat lost or gained
c = specific heat capacity
m = mass in g
$\Delta T = T_{\text{final}} - T_{\text{initial}}$

Units for specific heat capacity: J g^{-1} ^{o}C^{-1} or J g^{-1}K^{-1}

Molar Heat capacity

- **Molar Heat capacity** of a substance is its heat capacity per mole.

= **specific heat capacity x molar mass of substance**.

- Example: What is the molar heat capacity of water?

Molecular weight of water = 18 g mol^{-1}

Molar heat capacity = 4.184 J g^{-1} ^{o}C^{-1} x 18 g mol^{-1}

= **75.31 J mol^{-1} ^{o}C^{-1}**

Table: Specific Heat Capacities (*c*) of Some Elements, Compounds, and Materials

Substance	Specific Heat Capacity (J/g·K)	Substance	Specific Heat Capacity (J/g·K)
Elements		**Solid materials**	
aluminum, Al	0.900	wood	1.76
graphite,C	0.711	cement	0.88
iron, Fe	0.450	glass	0.84
copper, Cu	0.387	granite	0.79
gold, Au	0.129	steel	0.45

Compounds	Specific Heat Capacity (J/g·K)
water, $H_2O(l)$	4.184
ethyl alcohol, $C_2H_5OH(l)$	2.46
ethylene glycol, $(CH_2OH)_2(l)$	2.42
carbon tetrachloride, $CCl_4(l)$	0.862

DO NOT MEMORISE!

Example

- **Question**

A 22.05 g solid is heated in a test-tube to 100.00°C and added to 50.00 g of water in a coffee-cup calorimeter. The water temperature changes from 25.10°C to 28.49°C. Find the specific heat capacity of the solid.

- **Plan**

Since the water and the solid are in contact, heat is transferred from the solid to the water until they reach the same T_{final}.

In addition, the heat given out by the solid ($-q_{\text{solid}}$) is equal to the heat absorbed by the water (q_{water}).

- water

$\Delta T_{\text{water}} = T_{\text{final}} - T_{\text{initial}} = (28.49°\text{C} - 25.10°\text{C}) = \mathbf{3.39°C}$

OR

$\Delta T_{\text{water}} = T_{\text{final}} - T_{\text{initial}} = (301.64\text{ K} - 298.25\text{ K}) = \mathbf{3.39\ K}$

- solid

$\Delta T_{\text{solid}} = T_{\text{final}} - T_{\text{initial}} = (28.49°\text{C} - 100.00°\text{C})$

$= \mathbf{-71.51°C}$

OR

$\Delta T_{\text{solid}} = T_{\text{final}} - T_{\text{initial}} = (301.64°\text{C} - 373.15°\text{C})$

$= \mathbf{-71.51\ K}$

We know that

$$-q_{system} = q_{surrounding}$$

Therefore

$$-(c_{solid} \text{ x } \text{mass}_{solid} \text{ x } \Delta T_{solid}) = c_{Water} \text{ x } \text{mass}_{water} \text{ x } \Delta T_{water}$$

If we rearrange

$$c_{solid} = \frac{c_{Water} \text{ x } \text{mass}_{water} \text{ x } \Delta T_{water}}{-(\text{mass}_{solid} \text{ x } \Delta T_{solid})}$$

$$= \frac{4.184 \text{ J/g·K x } 50.00 \text{ g x } 3.39 \text{ K}}{-(22.05 \text{ g x } (-71.51 \text{ K}))}$$

$$\boxed{\mathbf{= 0.450\ J/g{\cdot}K}}$$

Determining the Enthalpy Change of an Aqueous Reaction

- **Question**

50.0 mL of 0.500 *M* NaOH is placed in a coffee-cup calorimeter at 25.00 ^{o}C and 25.0 mL of 0.500 *M* HCl is carefully added, also at 25.00 ^{o}C. After stirring, the final temperature is 27.21 ^{o}C. Calculate q_{soln} (in J) and the change in enthalpy, ΔH, (in kJ/mol of H_2O formed).

- Assumptions:

i. the total volume is the sum of the individual volumes,

ii. *density* = 1.00 g/mL and

iii. c = 4.184 J/g·K

- **Plan**

Heat flows from the reaction (the system) to its surroundings (the solution). Since $-q_{\text{rxn}} = q_{\text{soln}}$, we can find the heat of the reaction by calculating the heat absorbed by the solution.

(a) To find q_{soln}:

- Total mass (g) of the solution

= (25.0 mL + 50.0 mL) x 1.00 g/mL = 75.0 g

- ΔT_{soln} = 27.21 °C – 25.00°C = 2.21°C

OR ΔT_{soln} = 2.21 K (convert to Kelvin and subtract!)

$q_{\text{soln}} = c_{\text{soln}} \text{ x } \text{mass}_{\text{soln}} \text{ x } \Delta T_{\text{soln}}$

= (4.184 J/g·K)(75.0 g)(2.21 K

= 693.50 J

(b) To find ΔH_{rxn} we first need a balanced equation:

$$\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

For HCl:

$$25.0 \text{ mL HCl} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.500 \text{ mol}}{1 \text{ L}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol HCl}} = 0.0125 \text{ mol H}_2\text{O}$$

For NaOH:

$$50.0 \text{ mL NaOH} \times \frac{1 \text{ L}}{10^3 \text{ mL}} \times \frac{0.500 \text{ mol}}{1 \text{ L}} \times \frac{1 \text{ mol H}_2\text{O}}{1 \text{ mol NaOH}} = 0.0250 \text{ mol H}_2\text{O}$$

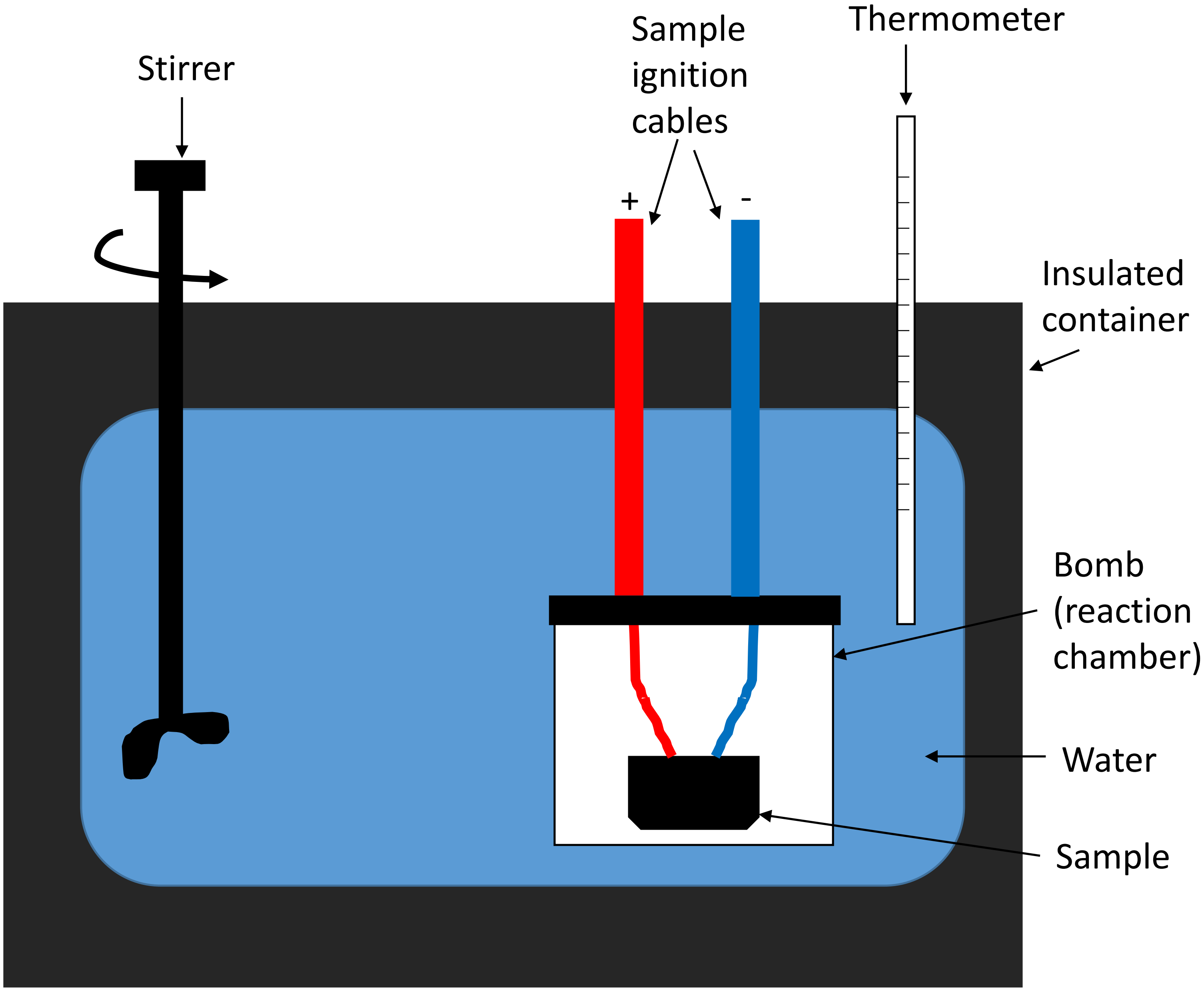
HCl is limiting, and the amount of H_2O formed is 0.0125 mol.

$$\Delta H_{\text{rxn}} = \frac{q_{\text{rxn}}}{\text{mol H}_2\text{O}} = \frac{-693 \text{ J}}{0.0125 \text{ mol}} \times \frac{1 \text{ kJ}}{10^3 \text{J}} \boxed{\mathbf{= -55.4 \text{ kJ/mol H}_2\text{O}}}$$

Bomb calorimeter

- Constant volume, heat released corresponds to q_v
- A bomb calorimeter structure consists of the following:

1. Steel bomb which contains the reactants
2. Water bath in which the bomb is submerged
3. Thermometer
4. A motorized stirrer
5. Wire for ignition


Stirrer
Sample ignition cables
+
-
Thermometer
Insulated container
Bomb (reaction chamber)
Water
Sample

NOTE

- The volume is constant
- What is measured is really ΔE, not ΔH.
- For most reactions, the difference is small.
- The heat absorbed (or released) by the water is very good approximation of the enthalpy change for the reaction.

Bomb calorimetry

$q_{V,system} + q_{V,surrounding} = 0$

$q_{V,\ surrounding} = q_{bomb} + q_{water}$

Where $q_{bomb} = C\Delta T$

Where $q_{water} = m_{water}c_{water}\Delta T$

Example

- **Question**

A 0.4440 g sample of sucrose ($C_{12}H_{22}O_{11}$) is burned in a bomb calorimeter and the temperature increases from 20.00 °C to 22.06 °C. The calorimeter contains 748.0 g of water, and the bomb has a heat capacity of 420.0 J/°C. Calculate ΔE for the combustion reaction in kJ/mol.

ΔT = 22.06 °C – 20.00°C = 2.06

$q_{V,\ \text{surrounding}}$ = q_{bomb}+ q_{water}

= (420.0 J/°C x 2.06) + (748 g x 4.18 J/°C x 2.06)
= 7306.078 J

Where q_{bomb} = (420.0 J/°C x 2.06)
Where q_{water} = 748 g x 4.18 J/°C x 2.06

$$\Delta E = \frac{q_{V,\mathrm{combuction}}}{n}$$

$$n = \frac{0.444\,\mathrm{g}}{342.34\,\mathrm{g\,mol^{-1}}} = 0.001295\,\mathrm{mol}$$

$$\Delta E = \frac{-7306.078\,\mathrm{J}}{0.001295\,\mathrm{mol}} = -5.64176\,\mathrm{x}10^{6}\,\mathrm{J\,mol^{-1}}$$

$$\Delta E = -5641.76\,\mathrm{x}10^{3}\,\mathrm{kJ\,mol^{-1}}$$